Chemical fingerprinting of unevaporated automotive gasoline samples

P.M.L. Sandercock[*], E. Du Pasquier

Centre for Forensic Science, University of Technology, P.O. Box 123, Sydney, Broadway NSW 2007, Australia

Abstract

The comparison of two or more samples of liquid gasoline (petrol) to establish a common origin is a difficult problem in the forensic investigation of arsons and suspicious fires. A total of 35 randomly collected samples of unevaporated gasoline, covering three different grades (regular unleaded, premium unleaded and lead replacement), were examined. The high-boiling fraction of the gasoline was targeted with a view to apply the techniques described herein to evaporated gasoline samples in the future.

A novel micro solid phase extraction (SPE) technique using activated alumina was developed to isolate the polar compounds and the polycyclic aromatic hydrocarbons (PAHs) from a 200 µl sample of gasoline. Samples were analysed using full-scan gas chromatography–mass spectrometry (GC–MS) and potential target compounds identified. Samples were then re-analysed directly, without prior treatment, using GC–MS in selected ion monitoring (SIM) mode for target compounds that exhibited variation between gasoline samples. Principal component analysis (PCA) was applied to the chromatographic data. The first two principal components (PCs) accounted for 91.5% of the variation in the data. Linear discriminant analysis (LDA) performed on the PCA results showed that the 35 samples tested could be classified into 32 different groups.
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1. Introduction

Interpretation of forensic evidence and, in particular, the ability to uniquely identify petroleum products is a crucial challenge in the scientific investigation of arson. Limitations in this area are having a significant impact on police investigations and the successful prosecution of arson cases. Gasoline is the most commonly used liquid accelerant in arson [1–3]. In situations where incendiary bombs (petrol bombs) or gasoline delayed-ignition devices are used there is often sufficient liquid gasoline recovered from the scene to allow a comparison to be made with gasoline seized from the suspect and with other sources of gasoline. The ability to chemically fingerprint gasoline would allow different gasoline samples to be distinguished from one another, and would allow the police to establish conclusive links between a suspect and a fire scene.

A number of studies have demonstrated that, in some cases, gasoline samples taken from different service stations and/or refineries can be distinguished from each other. Some of these studies relied primarily on differences in tetraalkyl lead content and showed good discrimination between samples of unevaporated gasoline [4–6]. Leaded gasoline has been banned from most industrialised countries around the world making comparisons based on tetraalkyl lead compounds out of date [7]. Other researchers have used differences in the hydrocarbon profile of gasoline to differentiate between samples [1,6,8–13]. As noted in the work of Mann [1], the reliance on the more volatile components of gasoline for establishing differences between samples prevents comparisons from being made between samples evaporated by more than 50%.

The examination of finished gasoline for less volatile trace compounds provides one avenue for its characterisation that has not been reported in the literature. The introduction of different trace species during the refining and blending processes that occur in a refinery may introduce detectable differences between batches of finished gasoline. Two generic groups of trace organic compounds, polar

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[*] Corresponding author. Fax: +61-780-495-6961.
E-mail address: mark.sandercock@rcmp-grc.gc.ca (P.M.L. Sandercock).

compounds and polycyclic aromatic hydrocarbons (PAHs), were considered in this study for their potential to be used in the identification of batch to batch variations in gasoline. It is also thought that the lower volatility of these compounds may also allow them to be used in the comparison of evaporated gasoline samples.

1.1. Polar compounds

A few articles have reported that the C_0–C_4-alkylphenols are present in varying relative concentrations in crude oil [14–16]. These compounds have been used as markers for characterising crude oil spills in aqueous environments due to the solubility of the phenols in water [17]. It is proposed here that the polar compounds present in a crude oil may survive the refining process and might be suitable markers for differentiating between samples of gasoline.

Significant interest in detecting polar compounds such as phenols and amines in gasoline arose during the 1980s and led to a number of articles being published on this topic. Polar compounds are present in finished gasoline in relatively low concentrations and so it is necessary to extract them from the complex petroleum matrix prior to analysis by gas chromatography. Both liquid–liquid extraction methods (i.e. partitioning) [18–20] and solid phase extraction (SPE) on an adsorbent such as silica gel have been used to recover these compounds from gasoline [21–23]. Solid phase extraction is the use of a solid adsorbent to separate analytes of interest from a complex mixture. This technique has been applied successfully over the decades to the problem of separating a large variety of target analytes from complex mixtures in solution. In the past, silica gel and alumina have been the most popular of the strongly polar adsorbents for solid phase extractions of complex mixtures [24]. Both of these adsorbents show similar preferential adsorption of polar organic compounds. One significant difference between these two adsorbents is the preference of alumina to adsorb acidic compounds such as phenols, whilst silica has a preference to adsorb basic compounds such as aliphatic amines [24]. Alumina is generally considered to be basic in nature, while silica gel is considered to be acidic [25], and it has been shown that alumina has a greater affinity than silica gel for acidic compounds such as alkylphenols [25]. For some weak organic bases such as aniline, silica gel does not necessarily exhibit greater adsorption than alumina [25]. In this study, alumina was selected for the SPE of polar compounds from gasoline.

1.2. Polycyclic aromatic hydrocarbons

In 1977, Mach [26] reported the use of gas chromatography–mass spectrometry (GC–MS) to examine polycyclic aromatic hydrocarbons in severely evaporated and burned samples of gasoline. Mach concluded that specific PAHs present in gasoline are unique to this type of petroleum product and may be a point of comparison to determine the presence or absence of gasoline in a fire debris sample. Later, Hennig [27]

examined three gasoline samples, each from a different refinery. Hennig found that the relative concentration of the higher boiling compounds was dependant on the refinery that produced the gasoline. Work done by Thatcher [28] on gasoline from three Australian refineries supported the results of Hennig. Thatcher found that in samples of regular and premium gasoline, the relative amounts of certain PAHs were dependent on the refinery that made the gasoline. Thatcher found that, in particular, the relative amounts of naphthalene, 1,2-dimethylnaphthalene, and phenanthrene could be used to distinguish all six gasoline samples (three regular and three premium). The significance of examining the higher boiling compounds such as the PAHs is that these compounds will remain even if the gasoline has been evaporated, thus providing the possibility of comparing gasoline samples that have undergone a significant amount of evaporation.

It is possible for crude oil obtained from a single oil field to exhibit variation in the relative amounts of the alkylated polycyclic aromatic hydrocarbons. Radke et al. studied six crude oil samples taken at different depths from five wells in the Handil oil field, Indonesia [29]. They observed some differences between samples in the relative ratios of the methylnaphthalenes and the dimethylnaphthalenes. The use of PAHs to identify the source of a crude oil spill has been described by Wang and Fingas [30] and is the subject of a review [31]. The high boiling, alkylated PAHs in particular are good for fingerprinting oils because they are persistent in the environment after a spill has occurred. The polycyclic aromatic hydrocarbons typically examined in the investigation of environmental spills include naphthalene, phenanthrene, fluorine, chrysene, dibenzothiophene and their alkylated homologues [30]. Wang and Fingas [32] have shown that different crude oils will have different distributions of PAHs and their alkylated homologues, including aromatic sulphur compounds such as the methyldibenzothiophenes. Aromatic sulphur compounds have received attention in crude oil comparisons because unrefined oils tend to vary significantly in their sulphur content [32,33]. Differences in the relative amounts of organo-sulphur compounds in gasoline have been reported, [34] while a more recent article indicated that the chromatographic patterns of gasoline samples can be quite similar [35]. It is doubtful that aromatic sulphur compounds will be helpful in the characterisation of refined fuels because these compounds are being intentionally refined out of the finished petroleum product. Industrialised countries and regions around the world are actively decreasing the allowable concentration of organic sulphur compounds in gasoline, a trend that has been summarised in *The Worldwide Fuel Charter* [36].

The process of refining crude oil into gasoline not only intentionally removes certain products such as the organosulphur compounds, but it also removes most high molecular weight compounds, thus significantly reducing the concentration of two- and three-ring PAHs (i.e. alkylnaphthalenes and alkylphenanthrenes) and eliminating completely the four-ring PAHs (i.e. chrysene). Thus, it is to be expected

that the refining process will remove much of the chemical information that makes one crude oil different from another. Although finished petroleum products such as gasoline may retain trace amounts of two- and three-ring PAHs, the amount of information held by these compounds is expected to be reduced relative to the crude oil from which it originated. If the differences in PAHs between crude oils were to persist through the refining process then it might be possible to differentiate gasoline samples based on the relative ratios of the polycyclic aromatic hydrocarbons.

In order to evaluate the possibility of using PAHs for characterising a gasoline sample it was desirable to first isolate all of the PAHs that are present using solid phase extraction. It has long been known that activated alumina is well suited to adsorbing and separating aromatic hydrocarbons [37] and, in particular, fused polycyclic aromatic hydrocarbons [38,39]. The suitability of alumina for the separation of aromatic compounds is due, in part, to the planar or near planar nature of many aromatic and PAHs which are retained by the planar geometry of the alumina crystal structure [40,41]. The use of solid phase extraction to recover trace analytes from complex fuel matrices has been described for synthetic fuels using alumina [42–44]. Bundt et al. reported a solid phase extraction method using a silica gel column to separate aliphatics, monoaromatics, diaromatics, polyaromatics and polar compounds in diesel fuels from one another [45]. Song and Lai reported the fractionation of alkyl-substituted benzenes and polycyclic aromatics hydrocarbons from jet fuel on an alumina column [42,43]. In this study, alumina was chosen over silica gel as the adsorbent because alumina is better suited for the extraction of polycyclic aromatic hydrocarbons.

1.3. Research aims

An examination of the scientific literature has indicated that the analysis of liquid gasoline for trace polar and polycyclic aromatic hydrocarbons may allow one sample of gasoline to be differentiated from another. The aim of this research is to use micro solid phase extraction techniques and GC–MS to extract and identify, respectively, the trace polar and PAH compounds that are present in gasoline. The analytical results will be used to determine which, if any, of these compounds may be used to differentiate between samples of unevaporated gasoline.

2. Materials and methods

2.1. Samples

Thirty-five samples of gasoline were obtained from service stations in metropolitan Sydney, Australia (Table 1) over a 7-month period (March–September 2001). The majority of the samples (29) were collected over a period of 7 weeks (March–April 2001). Each sample collected was stored in the

Table 1
Summary of 35 unleaded gasoline samples collected between March and September 2001

No.	Sample	Date[a]	Brand[b]	Grade[c]
1	RU02	13.03	Shell (1)	Regular
2	LR06	13.03	Shell (1)	Lead Rep
3	PU07	13.03	Shell (1)	Premium
4	RU11	29.03	Shell (1)	Regular
5	PU12	29.03	Shell (1)	Premium
6	RU13	05.04	Shell (1)	Regular
7	RU14	18.04	Caltex (2)	Regular
8	RU15	18.04	Mobil (3)	Regular
9	RU16	18.04	Caltex (4)	Regular
10	PU17	18.04	Caltex (4)	Premium
11	RU18	18.04	Shell (5)	Regular
12	PU19	24.04	BP (6)	Premium
13	RU20	24.04	BP (6)	Regular
14	RU21	24.04	Caltex (7)	Regular
15	RU22	24.04	Shell (8)	Regular
16	RU23	24.04	BP (9)	Regular
17	RU24	24.04	Mobil (10)	Regular
18	RU25	24.04	Mobil (11)	Regular
19	RU26	24.04	Caltex (12)	Regular
20	RU27	24.04	Shell (13)	Regular
21	PU28	24.04	Shell (13)	Premium
22	RU29	24.04	BP (14)	Regular
23	RU30	24.04	BP (15)	Regular
24	PU31	24.04	Shell (16)	Premium
25	RU32	24.04	Shell (16)	Regular
26	RU33	24.04	Mobil (17)	Regular
27	RU34	24.04	Mobil (18)	Regular
28	RU35	24.04	Mobil (19)	Regular
29	RU36	28.04	BP (20)	Regular
30	PU37	14.08	BP (21)	Premium
31	RU38	14.08	BP (22)	Regular
32	PU39	12.09	Burmah (23)	Premium
33	RU40	12.09	Burmah (23)	Regular
34	PU41	12.09	Woolworths (24)	Premium
35	RU42	12.09	Woolworths (24)	Regular

[a] Date is expressed as day and month (dd.mm).

[b] Number in parentheses indicates the service station from which a sample was taken (e.g. Shell (1) is Shell brand gasoline taken from service station location number 1, Caltex (2) is Caltex brand gasoline taken from service station location number 2, etc.).

[c] The three grades of unleaded gasoline are: regular, premium and lead replacement.

dark at room temperature in a 125 ml amber, Boston round glass bottle sealed with a polypropylene cap fitted with a teflon-faced foamed polyethylene liner (Wheaton).

2.2. Solid phase extraction

Reagent grade petroleum spirit (bp 30–40 °C, Univar), spectrophotometric grade *n*-pentane (Aldrich), HLPC grade dichloromethane (BDH) and HPLC grade methanol (EM Science) were used for SPE without further treatment. Micro-columns were made by sandwiching 1.0 g of neutral

alumina (Merck) between two plugs of silanised glass wool (Alltech) in a 14.6 cm (5.75 cm) Pasteur pipet (MapleLeaf). Alumina micro-columns were stored in an oven at 60 °C and were pre-heated to 110 °C for 1 h prior to use [46,47].

The procedure devised by Bundt et al. for the SPE of diesel fuel using silica gel was modified for use with gasoline using alumina [45]. While still warm the column was conditioned by washing with 2 ml petroleum spirit. A 200 μl aliquot of the gasoline sample was diluted with 0.8 ml petroleum ether and the solution transferred to the head of the column. The aliphatic and monoaromatic compounds were eluted from the column with 5 ml petroleum spirit followed by 4 ml of a solution of 5% dichloromethane in n-pentane (v/v). The first fraction, containing the polycyclic aromatic hydrocarbons, was eluted with 4 ml of a solution of 10% dichloromethane in n-pentane (v/v). The second fraction, containing the polar compounds, was eluted from the column with 2 ml methanol. The volume of each fraction was reduced to approximately 0.25 ml under a gentle stream of dry nitrogen, and then immediately transferred to a gas chromatography vial fitted with a conical glass insert and capped. Each sample was extracted in triplicate.

2.3. Gas chromatography–mass spectrometry

Gas chromatography was performed on a 30 m × 0.25 mm i.d. × 0.25 μm film HP5-ms capillary column using an Agilent 6890 gas chromatograph connected to an Agilent 5973 mass selective detector (MSD).

2.4. Analysis of extracts

Polycyclic aromatic hydrocarbon extracts (first fraction) were analysed using the following chromatographic conditions: split injection (3:1) at 280 °C; temperature programmed from 40 (3 min isothermal) to 208 °C at 4 °C/min, then to 290 °C at 25 °C/min (held for 5 min); helium carrier gas at a constant flow rate of 1.2 ml/min. Polar extracts (second fraction) were analysed by gas chromatography–mass spectrometry without chemical derivatisation of the phenolic compounds [14,27,28]. Chromatographic conditions were as follows: split injection (3:1) at 280 °C; temperature programmed from 40 (3 min isothermal) to 105 °C at 2 °C/min, then to 290 °C at 20 °C/min (held for 5 min); helium carrier gas at a constant flow rate of 1.2 ml/min. For the analysis of both the PAH and polar extracts the sample injection volume was 1 μl, and the detector was operated in full-scan mode (30–350 amu) with a sampling rate of 4.45 scans/s.

2.5. Selected ion monitoring of polycyclic aromatic hydrocarbons

Samples were prepared for GC–MS analysis using SIM by diluting an aliquot of neat gasoline with dichloromethane (1:4, v/v). The conditions set for the gas chromatograph and detector were modified according to the PAH compounds

Table 2
Selected ion fragments for each isomeric group of polycyclic aromatic hydrocarbons analysed in unleaded gasoline samples

	m/z^+
Two-ring	
C_0-naphthalene	127, 128, 129
C_1-naphthalenes	139, 141, 142, 143
C_2-naphthalenes	127, 128, 141, 142, 155, 156, 157
C_3-naphthalenes	128, 141, 142, 155, 156, 169, 170, 171
Three-ring	
C_0-anthracene	178
C_0-phenanthrene	178
C_1-phenanthrene	192
C_2-phenanthrene	206

being detected. For the two-ring PAHs the same gas chromatograph conditions used for the analysis of the PAH extracts (first fraction) were applied except that the split ratio was increased to 50:1. The detector was set to monitor the following ions: m/z^+ 127, 128, 141, 142, 155, and 156 (50 ms dwell time). A second method for the analysis of the two-ring PAHs by SIM was devised whereby the gas chromatograph conditions remained unaltered except that the split ratio was decreased to 15:1, and the detector was set to monitor the following ion groups: m/z^+ 127, 129, 139 and 143 (group 1); m/z^+ 128, 141, 142, 155, 156 and 157 (group 2); m/z^+ 128, 141, 153, 155, 169, 170 and 171 (group 3). Dwell times were 100 ms for group 1 and 50 ms for groups 2 and 3. For the three-ring PAHs the GC conditions remained unchanged except that the split ratio was decreased to 2:1, and the detector was set to monitor the following ions: m/z^+ 178, 192 and 206. Ion fragments and their corresponding PAH isomer group are given in Table 2. In all cases five aliquots from each sample were analysed.

2.6. Data analysis

Peak area information was extracted from integrated chromatograms using a macro written specifically for this study using the instrument software (HP ChemStation®). Data was loaded and parsed into a spreadsheet (Excel, MicroSoft®) and all integration results obtained from the macro were checked manually. The data was normalised using a natural logarithmic transformation [48]. Principal component analysis (PCA) and linear discriminate analysis were performed using statistical software (Minitab®).

3. Results and discussion

3.1. Polar compounds

For the thirty-five gasoline samples extracted (in triplicate) by micro SPE, visual inspection of the gas chromatograms did

Table 3
Isomeric groups of polycyclic aromatic hydrocarbon identified in unleaded gasoline samples

Two-ring	Three-ring
C_0-naphthalene	C_0-fluorene
C_1-naphthalenes	C_1-fluorenes
C_2-naphthalenes	C_2-fluorenes
C_3-naphthalenes	C_0-anthracene
	C_0-phenanthrene
	C_1-phenanthrenes
	C_2-phenanthrenes

not reveal any significant differences between samples in the relative ratios of the polar compounds. In some cases the presence of the oxygenate ethanol was sufficient to cause the majority of the polar compounds to elute from the micro-column immediately after the introduction of the sample onto the head of the column. In these samples only a small concentration of the polar compounds was retained on the column and subsequently recovered for analysis.

3.2. Polycyclic aromatic hydrocarbons

Micro solid phase extraction was performed on each of the 35 gasoline samples in triplicate and the PAH extracts analysed by gas chromatography were found to be reproducible for each sample. The PAHs present in each of the 35 gasoline samples was found to be very consistent. Table 3

Table 4
Results of PCA of C_0–C_2-naphthalenes by GC–MS (SIM)

	Eigen value	Proportion	Cumulative (%)
PC1	8.4765	0.771	77.1
PC2	1.5857	0.144	91.5
PC3	0.7925	0.072	98.7
PC4	0.0714	0.006	99.3
PC5	0.0466	0.004	99.8

lists the isomeric groups of the two- and three-ring PAHs found in each of the 35 gasoline samples.

The precision of the GC analysis for the C_0–C_2-naphthalenes was good. However, some gasoline samples had very low concentrations of the C_2-naphthalenes relative to the C_0- and C_1-naphthalenes, which resulted in lower precision for the peak area integration results. To overcome this problem a new approach was attempted whereby the signal for the C_0- and C_1-naphthalenes was reduced by selectively monitoring the less abundant ions for these compounds, whilst continuing to monitor the most abundant ions for the C_2-naphthalenes. Thus, the split ratio could be decreased to allow more of the C_2-naphthalenes to be injected onto the column, but the signal of the C_0- and C_1-naphthalenes was reduced sufficiently to prevent the detector from overloading (Fig. 1). Good precision in the integration results for the C_0–C_2-naphthalenes was obtained using this technique.

The GC data was analysed by principal component analysis. The variation described by the first five principal
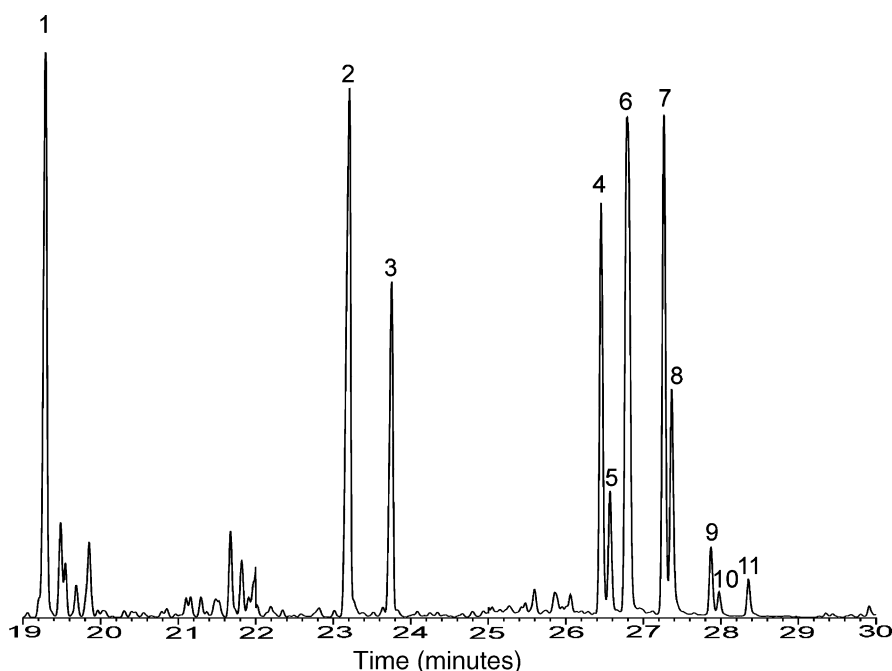

Fig. 1. Chromatogram of C_0–C_2-naphthalenes obtained by selected ion monitoring of the three isomer groups. GC–MS conditions given in Section 2. Peak assignments are given in Table 7.
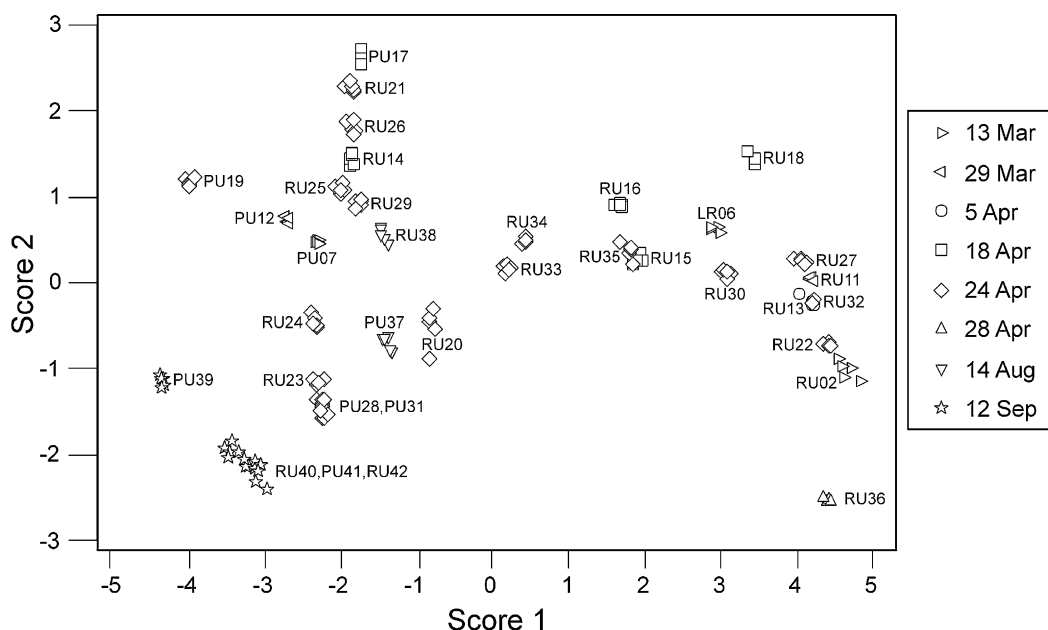
Fig. 2. PC score plot of 35 unleaded gasoline samples collected between March and September 2001 from 24 service stations in metropolitan Sydney, Australia. Data labels refer to samples described in Table 1.

components (PCs) is given in Table 4. The first two PCs represent 91.5% of the variation in the data. From the score plot of the first two PC scores (Fig. 2) it can be seen that the majority of the gasoline samples can be distinguished using this technique.

Using the first three PCs, linear discriminant analysis (LDA) with cross-validation correctly classified 168 of the 175 chromatograms (96%) by sample. In practical terms any overlap of one chromatogram (i.e. aliquot) from one gasoline sample with a chromatogram from another sample would cause these two samples to be indistinguishable. Therefore, the LDA results were re-examined and it was found that the 35 samples could be divided into 32 unique groups. Thirty of these groups each contained a single sample (i.e. five aliquots from one sample per group). The five remaining (misclassified) samples were divided between the two remaining groups. Two of these five samples formed a single

group (i.e. RU15 and RU35), while the other three samples formed another group (i.e. RU40, PU41 and RU42) (Table 5).

Visual inspection of the chromatograms of the PAHs showed clear differences between samples in the relative amounts of the C_0–C_2-naphthalenes (two-ring PAHs), as well as differences in the relative amounts of anthracene, and the C_0–C_3-phenanthrenes (three-ring PAHs). Although the PAH extractions were reproducible, it was found that the precision in the peak area integrations was not sufficient to give good clustering of individual samples after principal component analysis. In order to improve the analytical precision, GC–MS selected ion monitoring (SIM) was employed to analyse for the two- and three-ring PAHs directly. Although the precision between replicates was improved when analysing the PAHs, the precision for the three-ring PAHs was still unsatisfactory. The concentration of anthracene and phenanthrene were determined by

Table 5
Results of LDA with cross-validation

Predicted group	True group				
	RU15	RU35	RU40	PU41	RU42
RU15	3	1	0	0	0
RU35	2	4	0	0	0
RU40	0	0	3	0	1
PU41	0	0	0	5	1
RU42	0	0	2	0	3

Values in italic collectively indicate the five misclassified samples.

Table 6
Concentration of naphthalene, phenanthrene and anthracene in 35 unevaporated gasoline samples

	Concentration (µg/l)		
	Naphthalene	Phenanthrene	Anthracene
n	175	175	175
Samples	35	35	35
Mean	1006	15	7
S.D.	336	8	8
Minimum	392	5	1
Maximum	1880	42	41

Table 7
Retention indices for C_0–C_2-naphthalenes by GC–MS (SIM)

No.	Compound	PAH retention index		n-Alkane retention index	
		Lee et al. [49]	This work	Lai and Song [43]	This work
1	Naphthalene	200.00	200.08 ± 0.012	1179.7	1179.6 ± 0.06
2	2-Methylnaphthalene	218.14	221.22 ± 0.030	1290.5	1290.6 ± 0.16
3	1-Methylnaphthalene	221.04	224.31 ± 0.021	1306.8	1307.0 ± 0.12
4	2-Ethylnaphthalene	236.08	239.32 ± 0.003	1390.6	1390.0 ± 0.02
5	1-Ethylnaphthalene	236.56	239.92 ± 0.002	1393.8	1393.4 ± 0.01
6	2,6-Dimethylnaphthalene + 2,7-dimethylnaphthalene	237.58 + 237.71	241.13 ± 0.006	1400.9 + 1402.2	1400.2 ± 0.04
7	1,3-Dimethylnaphthalene	240.25	243.75 ± 0.003	1416.5	1415.4 ± 0.02
8	1,6-Dimethylnaphthalene + 1,7-dimethylnaphthalene	240.66 + 240.72	244.29 ± 0.003	1419.6	1418.7 ± 0.02
9	1,4-Dimethylnaphthalene + 2,3-dimethylnaphthalene	243.55 + 243.57	247.02 ± 0.003	1436.3	1435.0 ± 0.02
10	1,5-Dimethylnaphthalene	244.98	247.62 ± 0.002	1439.8	1438.4 ± 0.01
11	1,2-Dimethylnaphthalene	246.49	249.70 ± 0.004	1452.2	1450.6 ± 0.02

GC–MS (SIM) and found to be very low (Table 6). It is postulated that the low concentration of these compounds resulted in a large relative integration error, and so the desired analytical precision for the three-ring PAHs could not be obtained. The concentration of naphthalene was also determined for each sample (Table 6). It was found that the concentration of naphthalene (and by analogy, its methylated homologues) is significantly greater than that of the three-ring PAHs, and so attention was turned to these compounds.

The C_0–C_2-naphthalenes listed in Table 7 were identified by comparison to NIST standard mass spectra and by retention indices reported in the literature [43,49]. Retention indices were calculated using both an n-alkane system (n-C_5–n-C_{22}) [50] and a system based on the retention of

polycyclic aromatic hydrocarbon standards (naphthalene, phenanthrene and chrysene) [49]. The retention indices for the compounds shown in Table 7 were calculated from 75 chromatograms representing 15 samples.

The PCA results demonstrate that gasoline samples collected on the same day from different service stations can be distinguished from one another. For example, the five samples collected on 18 April 2001 were purchased from four different service stations within four blocks (approximately 400 m) of one another. These five samples are highlighted in the score plot in Fig. 3, in which it can be seen that each sample can be distinguished from one another. The 17 samples collected on 24 April 2001 were collected from 14 service stations in a different part of Sydney.
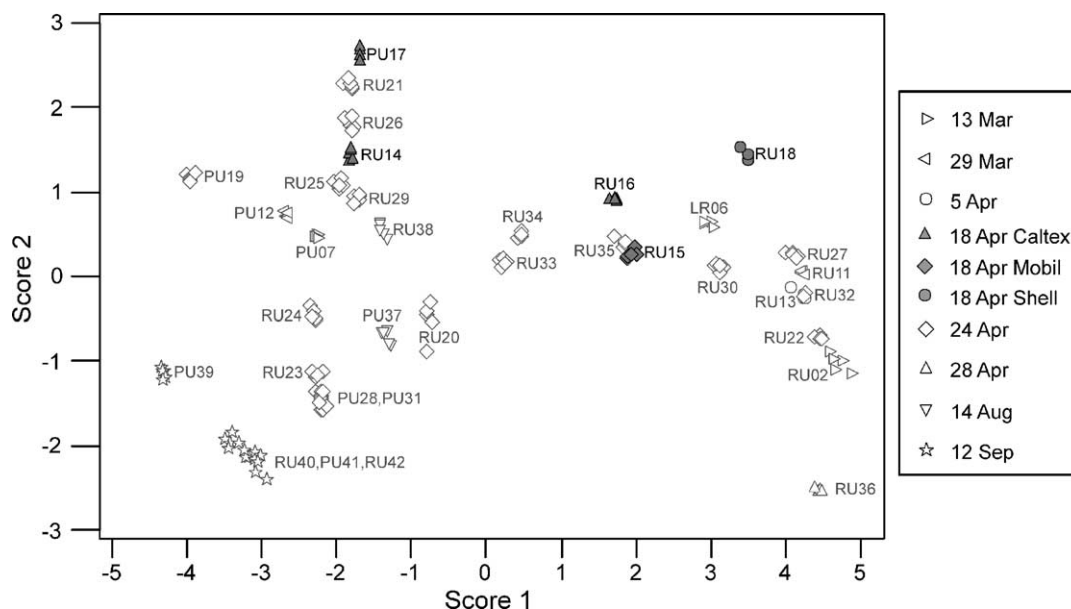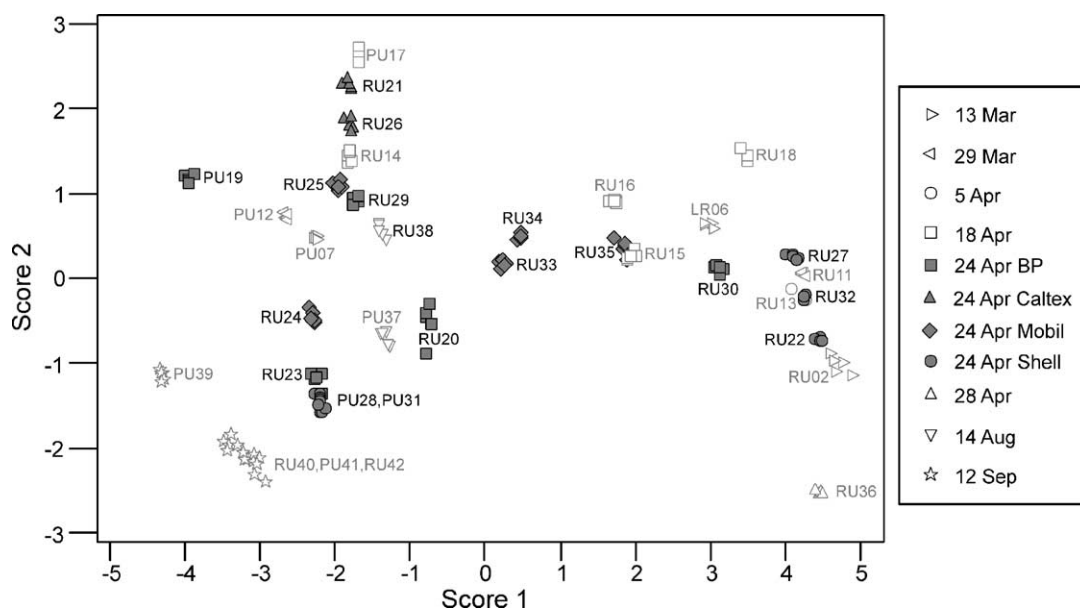

Fig. 3. PC score plot of 35 unleaded gasoline samples collected between March and September 2001 from 24 service stations in metropolitan Sydney, Australia. Five gasoline samples collected from four service stations on 18 April 2001 are hightlighted. Data labels refer to samples described in Table 1.

Fig. 4. PC score plot of 35 unleaded gasoline samples collected between March and September 2001 from 24 service stations in metropolitan Sydney, Australia. Seventeen gasoline samples collected from 14 service stations on 18 April 2001 are hightlighted. Data labels refer to samples described in Table 1.

These 14 stations were all within a 7 km radius from each other. Using the first three PCs, LDA (with cross-validation) correctly classified all 85 chromatograms (100%) by sample. These samples are highlighted in the score plot in Fig. 4, which shows good differentiation of the samples from each other.

A close inspection of the PCA results shows that all eight premium unleaded gasoline samples have a negative value for the first PC score (Fig. 5). This indicates that the refining process used to make these premium grade samples introduced a particular naphthalene profile. However, there is not
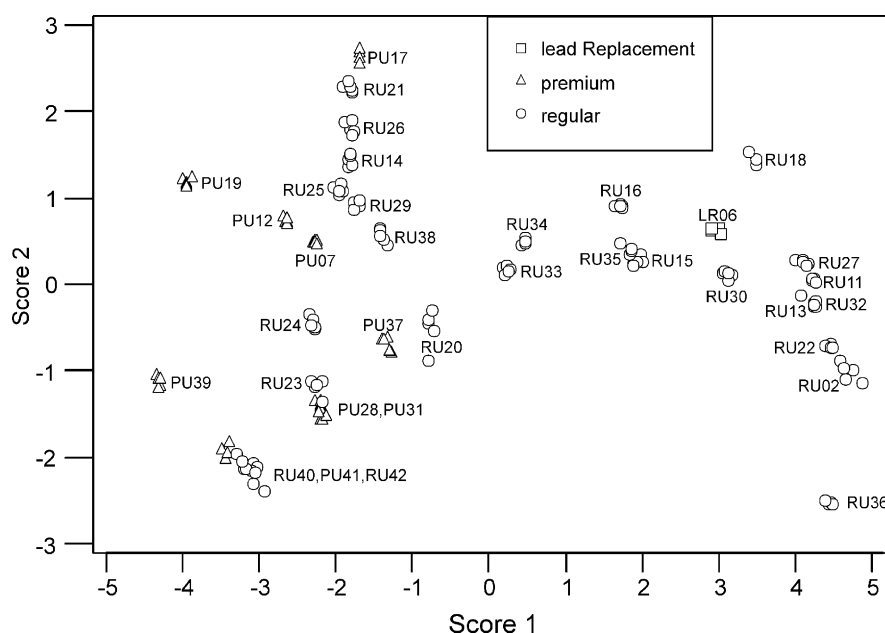

Fig. 5. PC score plot of 35 unleaded gasoline samples collected between March and September 2001 from 24 service stations in metropolitan Sydney, Australia. Sample designation by fuel grade (lead replacement, premium and regular). Data labels refer to samples described in Table 1.

enough information held in the naphthalene profile to allow the grade of the gasoline to be unequivocally assigned.

4. Conclusions

An investigation to extract and identify trace polar compounds and polycyclic aromatic hydrocarbons in 35 unevaporated gasoline samples has been conducted. The use of these trace compounds to differentiate one gasoline sample from another has been explored. It was found that the polar compound composition did not vary significantly from one sample to another and so these compounds were unsuitable for differentiating between samples of gasoline. Solid phase extraction of polycyclic aromatic hydrocarbons from different gasoline samples revealed that the PAH composition did vary from one sample to another. A GC–MS (SIM) method was developed to directly analyse for both two- and three-ring PAH compounds, however, the precision for the peak areas of the lower concentrations of the three-ring PAHs was not as high as for the two-ring PAHs. This resulted in the development of a one-step GC–MS (SIM) method that allowed the precise determination of the C_0–C_2-naphthalenes in unevaporated gasoline. It has been shown that these two-ring polycyclic aromatic hydrocarbons can be used to distinguish between different samples of gasoline.

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